Synthesis of Bis(quinoxalino) Ligand for the Removal of Transition Metal Contamination

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Abstract

Transition metal contamination is a constant environmental concern. One way to deal with these contaminations is by use of peraza-crown macrocycles as ligands to remove these metals. Outlined here is a novel synthesis of a quinoxalino-containing peraza-crown macrocycle by use of Cbz/Troc/Boc-protecting groups.

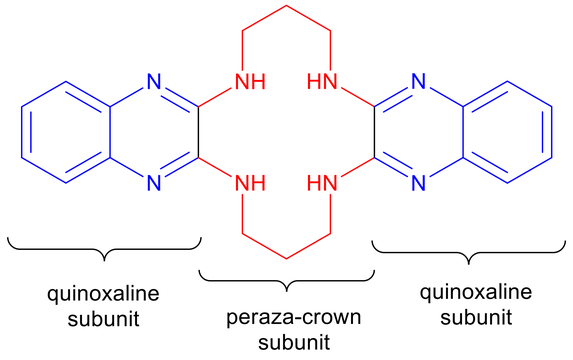

Figure 1

Introduction

Nitrogen-containing peraza-crown macrocycles with at least three nitrogen atoms are able to strongly complex with transition metals. The objective of our project is the synthesis of bis(quinoxalino) ligands which are capable of interacting with transition metals. We hypothesize that by coupling the rigidity of the quinoxaline and the good binding properties of the aza-crown macrocycle, we can obtain useful molecules with superior properties.

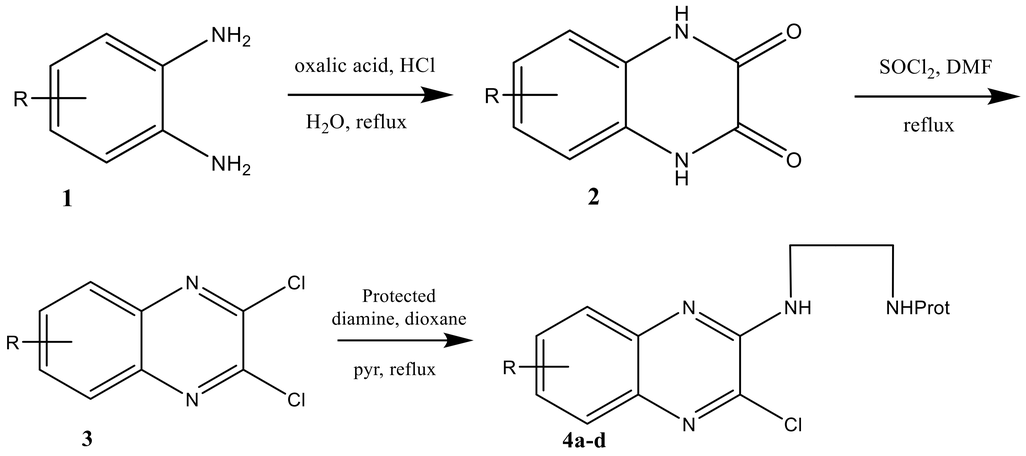

Figure 2

Results and Discussion

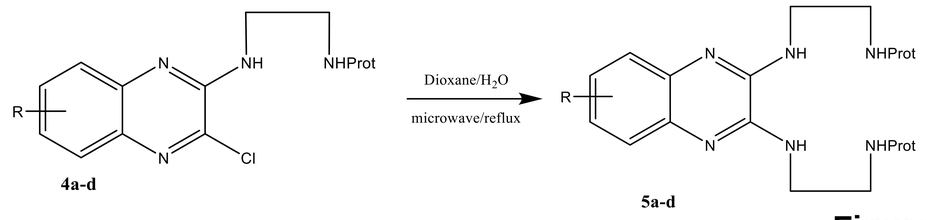

Figure 3

Oxalic acid in water was heated to 98°C, HCl and **1** were added. The temperature was maintained for 15 minutes to give **2**. The compound **2** was refluxed in $SOCl_2$ and DMF for 2 hours. **3** was obtained after workup. To obtain **4a-d**, the Cbz-protected diamine was dissolved in dioxane and basic pyridine. The **3** was added and the mixture was refluxed overnight. Additional substitutions from **3a-d** to **4a-d** have been attempted with a Troc and Boc protecting groups. Substitution of an additional protected amine to convert **4d** to **5d**. The compound **4** was dissolved in dioxane. Protected amine and a water/cesium carbonate solution were added. The mixture was microwaved at 160°C/100W for 1hr. The compound **5d** was produced in a small yield.

Entry	R	PG	Yield (2)	Yield (3)	Yield (4)	Yield (5)
a	H	Cbz	79%	83%	78%	-
b	4,5-dimethyl	Cbz	84%	97%	38%	-
c	H	Troc	-	-	78%	-
d	H	Boc	-	-	88%	22%

Summary and Future Work

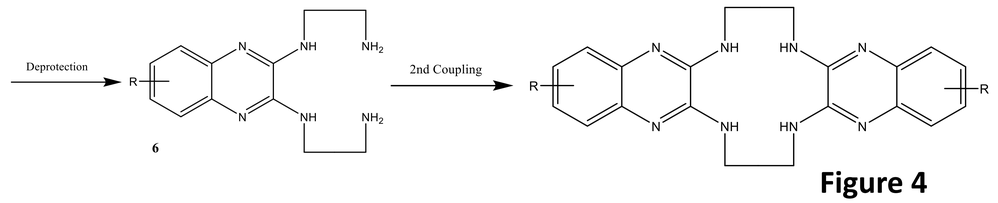

Figure 4

For our continued work, we will follow the synthesis as outlined in Figure 4. Synthesis of the compound **6** will be achieved by deprotection of **5**. This will then be coupled to another free quinoxaline subunit. Different peraza-crown macrocycles can be similarly synthesized by lengthening the diamine and by changing the R-groups. The final peraza-crown molecules will be tested for metal ion binding properties.